

# Flow injection analysis with amperometric detection for iodide determination as a tracer in seawater reservoirs

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**Abstract** In this study, an electrochemical method was developed using flow injection analysis and amperometric detection with screen-printed electrodes for iodide determination as a tracer in seawater reservoirs. The amperometric method resulted in a good linear correlation coefficient ( $r = 0.9966$ ) with a linear response over a concentration range of 1–10 mg L<sup>-1</sup>, a limit of detection of 0.2 mg L<sup>-1</sup> and a quantification of 0.6 mg L<sup>-1</sup>. In addition, the method has been shown to be precise, linear and homoscedastic. The recovery for the amperometric method was  $100 \pm 3 \%$ , and the recovery for the produced water samples fortified with iodide was  $102 \pm 2 \%$ . The amperometric method did not show interference from other anions. Thus, the proposed method is promising for analysing the iodide content of seawater reservoir samples with simple and inexpensive methodologies compared with ion chromatography techniques.

**Keywords** Iodide · Reservoir tracers · Amperometry · Screen-printed electrodes · Flow injection analysis

## 1 Introduction

Tracers are chemical species that can be detected in a fluid at very low concentrations that allow for tracing the flow of water [1]. Petroleum reservoir tracers, for example, are substances added to the injection fluid (usually water) and collected via sampling at production wells [2]. Tracers are increasingly being used in many scientific fields, including medicine, biology, physiology, nutrition, toxicology, biotechnology, chemistry, agriculture, geosciences and engineering. However, tracers are predominantly used for the characterisation of petroleum reservoirs [3]. In this case, they are used to monitor fluid distribution and trajectory, two parameters that are crucial for reservoir management and evaluation of the economic and environmental impact of petroleum production [2].

An effective reservoir tracer should be stable, unreactive with porous rock under the operating conditions and detectable at very low concentrations. Moreover, a tracer should be soluble in the aqueous phase, environmentally safe, easy to manipulate and inexpensive [2]. Iodide is an example of chemical tracer.

Iodine exists in more than one chemical form in seawater. It is distributed as iodide and iodate, with additional iodised organic compounds providing a small fraction of the bio-available iodine. The distribution of iodide in seawater varies with depth and geographical location. The total inorganic iodine concentration in seawater ranges from approximately 50 to 60 µg L<sup>-1</sup>, whereas the iodide concentration ranges from 30 µg L<sup>-1</sup> (near the shore or on the ocean surface and bottom waters) to below 1 µg L<sup>-1</sup> (in deep ocean water). Iodide is formed in seawater by the biologically mediated reduction of iodate and other reducing conditions. In fact, the redox cycle in which iodate and iodide are interconverted in surface waters has a profound effect on iodine levels in the oceans [4, 5].

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Developing a highly sensitive and selective method for iodide detection is challenging because iodate and iodide are present in the ocean at ultra-trace levels together with high concentrations of chloride. Detection of iodide in a seawater matrix is further complicated by high concentrations of carbonate and sulphate and the high ionic strength of seawater. Therefore, detection methods traditionally require a preliminary separation step to enrich iodide.

Over the last two decades, ion chromatography has been increasingly used for the determination of iodide content in seawater. Ito developed an ion chromatographic method with UV detection to quantify iodide and total inorganic iodine in seawater samples from Japan [6]. For iodide analysis, an anion-exchange resin with a polystyrene–divinylbenzene column was used for both the pre-concentration and separation of this ion. Seawater samples were filtered through a membrane and then passed through a concentrator column, and the trapped iodide was eluted with  $\text{NaClO}_4$ . To determine the total inorganic iodine, ascorbic and acetic acids were added to seawater samples to reduce iodate to iodide [6].

Another chromatographic method studied by Ito involved the use of a semi-microcolumn packed with high capacity anion-exchange resin made from a styrene–divinylbenzene copolymer; the mobile phase included  $\text{NaClO}_4$ ,  $\text{NaCl}$  and sodium phosphate buffer (pH 6.0). Using this method, the iodide present in seawater was concentrated on the column by both electrostatic and hydrophobic interactions and then eluted without peak broadening [7]. These chromatographic methods were useful in determining ultra-trace amounts of iodide; however, these methods often require a pre-concentration or separation step. Electroanalytical methods have also been used in detection systems combined with a separation technique such as chromatography for iodide determination.

Bruggink et al. developed a procedure for the detection of iodide in surface water using anion-exchange chromatography and pulsed amperometric detection. Detection of iodide was performed using a thin-layer cell equipped with a silver working electrode; the electrode surface participates in a precipitation reaction with iodide, resulting in the generation of a low anodic potential [8]. Rebarry et al. developed a procedure for the determination of iodide in edible salt using ion chromatography (without pre-treatment) with amperometric detection. The amperometric detector was composed of a silver working electrode in which the iodide combines with silver on the working electrode's surface to form a silver iodide precipitate. Silver is then oxidised in a process similar to that described by Bruggink [9]. Although the aforementioned chromatographic methods are highly sensitive, the instruments are very expensive and costly to maintain.

Electrochemical methods are commonly used to detect and measure analytes at low concentrations without prior separation because electrochemistry is inherently sensitive and selective. By taking advantage of the electroactivity of iodide, electrochemical methods have often been used to detect iodide. For example, Tian and Nicolas studied iodine speciation in the northwestern Mediterranean Sea. Iodide was determined using cathodic stripping square wave voltammetry with a polarographic analyser and a static mercury drop electrode. For total iodine quantification, a prior oxidation step with sodium hypochlorite solution was performed; measurements were taken via pulse differential voltammetry using the same electrode and a polarographic analyser. Because dissolved iodine exists in seawater in two oxidation states (iodide and iodate), the amount of iodate present was determined as the difference between iodide and the total iodine [10]. Although polarographic detection offers many advantages, such as low limits of detection and high sensitivities, the static mercury electrode is toxic and unsuitable for routine analysis.

The procedure proposed by Švancara et al. involves constant-current stripping analysis at a carbon-paste electrode containing tricresyl phosphate as a pasting liquid. This method was found to be selective for iodide determination in table salt because of a synergistic accumulation mechanism based on the ion-pairing and extraction of iodide in combination with electrolytic pre-treatment of the pasting liquid [11].

Bustin and Tomčík developed an interdigitated micro-electrode array sensor that has been used to determine the concentration of iodide in mineral water. This array-based system is based on reversible charge transfer of the redox system  $\text{I}_2/2\text{I}^-$  at a platinum microelectrode [12]. Chailapakul et al. [13] developed an amperometric method using flow injection analysis (FIA) and a boron-doped diamond thin film electrode (BDD) for determining iodide in nuclear emergency tablets.

FIA has been frequently applied in the quantification of several compounds present in samples with a diverse composition [14]. FIA systems offer excellent advantages because of certain characteristics, including the reproducibility of sample processing and transport to the detector (convective mass transport), leading to reproducible measurements, high sampling rates, simple and low cost manifolds, reagent and waste economy, and the possibility of automation. Furthermore, the use of an FIA system to transport samples to the detector in electroanalytical methods reduces the contact time between the sample and the electrode, minimising the adsorption effect [14]. Finally, the combination of FIA with electrochemical detection is attractive because of the flexibility of the former and the diagnostic power of the latter [15].

Screen printing technology is a well-established technique for the fabrication of chemical and biosensors [16]. Screen-printed electrodes (SPEs) offer a number of advantages over conventional electrodes. For instance, SPEs are suitable for working with microvolumes of material, are applicable for decentralised assays (point of care tests), are inexpensive, reproducible, of single use and can be mass-produced [17]. Moreover, screen-printed electrochemical sensors do not require pre-treatment such as electrode polishing or electrochemical pre-treatment via electro-deposition, which are commonly applied to other electrode materials. The adaptability of SPEs is also of great benefit in various areas of research; the ability to modify the electrodes with ease, through differing inks commercially available for the reference, counter, and working electrodes, allows for highly specific and finely calibrated electrodes to be produced for specific target analytes [16]. Finally, SPEs based on platinum present electrochemical characteristics similar to those of commercial platinum disc electrodes. Platinum disc electrodes and SPEs primarily differ in their microscopic behaviour, which is typical of microelectrodes and can be verified by chronocoulometry and voltammetry in experiments performed in the short time domain. This characteristic is associated with the high porosity of the electrode surface, which has been analysed by SEM [18].

Based on the aforementioned data in the literature, iodide is highly soluble at low temperatures, interacts minimally with porous rock and oxidises easily. Thus, we chose iodide as a chemical tracer for our experiments. In the present study, we used flow injection analysis with amperometric detection to measure iodide at very low concentrations using disposable SPE. Our results show that iodide can be used as a tracer in seawater reservoirs.

## 2 Experimental section

### 2.1 Reagents, apparatus and procedures

All chemicals were of analytical reagent grade (purchased from Merck), and doubly distilled water was used throughout. A stock solution of an iodide standard was prepared by dissolving a weighed amount of potassium iodide in water. Working solutions of iodide were obtained by diluting the stock solution in the supporting electrolyte, which was a 29 g L<sup>-1</sup> solution of sodium chloride. A real, produced water sample used in this study was previously analysed in duplicate by ion chromatography at Petrobras to obtain reference value.

All measurements were performed using an Autolab potentiostat, model PGSTAT 100, from Eco Chemie (Netherlands) with a current amplifier module controlled

by GPES 4.8 software. All experiments were performed at 25 °C.

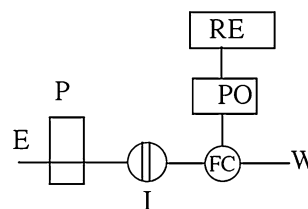
The iodide electroactivity and the selectivity of the electrochemical method were evaluated using a homemade platinum ultramicroelectrode (UME), with a diameter of 20 µm as the working electrode, and differential pulse and linear voltammetries. To prepare this electrode, a platinum wire with a diameter of 20 µm (purchased from Heraeus Vectra) was sealed directly into soft glass. Ag/AgCl/KCl (3 mol L<sup>-1</sup>) was used as the reference and counter electrode. The differential pulse voltammetry curves were performed with an amplitude of 15 mV, a step of 10 mV and a scan rate of 0.1 V s<sup>-1</sup> from 0.3 to 0.9 V versus Ag/AgCl. The linear voltammetry curves were performed using a 0.1 V s<sup>-1</sup> scan rate from 0 to 1 V versus Ag/AgCl.

The amperometric analyses using FIA were performed with the Drop Sense SPEs with a triple-electrode system consisting of a platinum working electrode, a Ag reference electrode and an auxiliary platinum electrode. A Millan four channel peristaltic pump (P) was used to provide a constant flow (1.5 mL min<sup>-1</sup>). The injection valve (I) was equipped with a 100 µL sample loop. A DropSens flow amperometric cell (FC) was used with a screen-printed electrode. The working electrode potential was set and controlled by a potentiostat (PO). FIA signals were recorded by the computer (RE). All tubes were made of silicon and were 0.5 in diameter. A diagram of the flow system is shown in Fig. 1.

The current versus time curves were obtained at 0.65 versus Ag/AgCl by injecting 1–10 mg L<sup>-1</sup> of iodide standard solutions containing 29 g L<sup>-1</sup> of chloride into the carrier stream, via the sample injection valve, to the electrochemical cell. The analytical curve was constructed by plotting the peak current versus iodide concentration.

### 3 Validation study

Validation of the amperometric method using FIA for the quantitative determination of iodide in produced water samples was performed via several steps, which were important to ensure the reliability of the obtained results [19, 20].



**Fig. 1** Scheme of the FIA apparatus for iodide determination

### 3.1 Selectivity

The selectivity of the electrochemical method was evaluated through analyses of samples containing  $100 \text{ mg L}^{-1}$  of different anions, including bromide, chloride, nitrite, sulphate, thiocyanate and fluoride (i.e. possible interferents). These analyses were performed using a platinum UME working electrode and the differential pulse voltammetry electrochemical technique.

### 3.2 Linearity

The linearity study was performed by evaluating the analytical curve constructed using 10 different concentrations of the iodide standard (from 1 to  $10 \text{ mg L}^{-1}$ ) containing  $29 \text{ g L}^{-1}$  chloride. The analysis was performed in triplicate for each concentration using a screen-printed electrode as the working electrode and amperometry as the electrochemical technique. The analytical curve (peak current vs. iodide concentration) was acquired by fitting the data obtained with iodide standard samples to the linear regression model. This curve was submitted to the Cochran test to evaluate the bilateral deviation of the variances to a 5 % significance level. The residue graph was generated from the differences between the values calculated from the straight line of the analytical curves and the values obtained experimentally.

### 3.3 Detection and quantification limits

The detection and quantification limits were also determined experimentally. Different concentrations of iodide ( $0.1$ ,  $0.2$ ,  $0.3$  and  $0.4 \text{ mg L}^{-1}$ ) were analysed in an electrochemical flow cell in order of decreasing iodide concentration. The experimental detection limit was obtained from the lowest current of iodide oxidation that was still significantly different from the baseline of the amperometric curve. The quantification limit was estimated as three times the detection limit.

### 3.4 Recovery

Standard solutions of iodide were prepared with concentrations ranging from 1 to  $10 \text{ mg L}^{-1}$ . Several aliquots were added into the flow electrolyte cell. The recovery method study was performed with these synthetic samples using the proposed amperometric method. A sample recovery study was also performed with real produced water samples fortified with  $2$ – $9 \text{ mg L}^{-1}$  iodide. The real produced water sample was analysed in triplicate by the amperometric method using FIA and compared with the value obtained by ion chromatography.

### 3.5 Precision

Precision was evaluated based on the repeatability of the analyses, which was analysed from the standard deviations obtained in triplicate from an analytical curve constructed with the same instrument.

### 3.6 Variances and residue analysis

The results of any quantitative method that can be described by a linear regression model should present analytical curves with significantly constant (homogenous) variances. This is called homoscedasticity. When these variances increase along with the concentration of the analysed species, the homoscedastic condition is violated (heteroscedasticity). The Cochran test was used to evaluate if the applied method was homo- or heteroscedastic. This test estimates the bilateral deviation of the variances at a 5 % significance level. The unique limitation for its use is the replication number, which should be equal for all measured series [19].

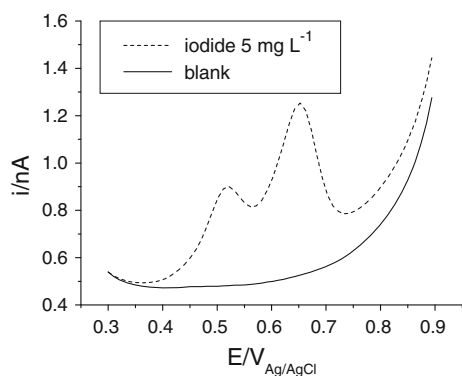
The residue is represented by the difference between the measured and model-predicted values. The residue analysis was evaluated to validate both the regression model and the variance behaviour [19]. A residual plot was prepared for each set of analyses.

### 3.7 Study of the matrix effect

The matrix effect is the effect on an analytical method caused by all the other components of the sample except the specific compound to be quantified. The matrix effect in the amperometric method was measured by statistical comparison of the analytical curves performed in synthetic iodide solution containing  $29 \text{ g L}^{-1}$  of chloride and in produced water.

### 3.8 Comparison of different analytical curves

To evaluate the slope of the two analytical curves, which were obtained from distinct matrixes, a sequence of statistical calculations was necessary. First, the residual variance ( $Se^2$ ) was determined for each analytical curve [19, 20]. Then, the Snedecor test was applied to verify if residual variances were significantly different [19, 20]. When the calculated  $F$  value ( $F_{cal}$ ) is lower than the critical  $F$  value ( $F_{crit}$ ), the variances can be considered statistically equivalent. In the second step, the grouped variance was calculated for each calibration curve. In the last step, the calculated  $t$  value ( $t_{cal}$ ) was obtained [19, 20] and compared with the critical  $t$  value ( $t_{crit}$ ) for a 5 % significance level. If  $t_{cal}$  is lower than  $t_{crit}$ , then the slopes of the two calibration curves can be considered statistically equivalent.

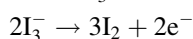
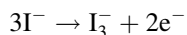


**Fig. 2** Voltammograms obtained by differential pulse voltammetry in the absence and the presence of iodide using Pt UME

## 4 Results and discussion

### 4.1 Electroactivity

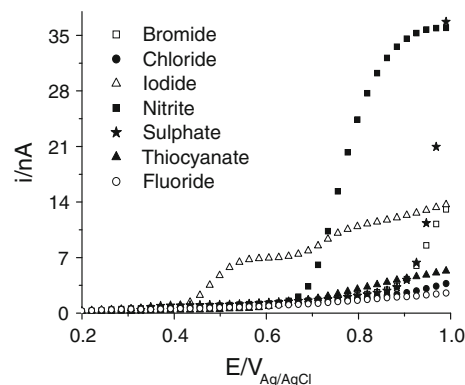
The electroactivity of iodide was investigated over a potential range of 0.3–0.75 V versus Ag/AgCl. Figure 2 shows the voltammograms obtained in the absence and presence of 5 mg L<sup>-1</sup> of iodide. In these voltammograms, two peaks at approximately 0.5 and 0.65 V versus Ag/AgCl were observed and correlated with two anodic processes. Hanson and Tobias [21] investigated iodide oxidation by cyclic voltammetry using platinum as the working electrode. In this study, the authors suggested that the oxidation sequence of iodide could be represented by the following reactions:



This mechanism was confirmed using UV–Visible spectroscopy in conjunction with cyclic voltammetry experiments. The peak current of these two peaks is proportional to the iodide concentration, allowing the correlation of analytical signals and iodide concentration.

### 4.2 Selectivity

Figure 3 shows the electrochemical behaviour of some interferent anions. The iodide electroactivity was compared with the electrochemical behaviour of these interferent anions (bromide, chloride, nitrite, sulphate, thiocyanate and fluoride). Not all anions showed electroactivity in the range from 0.3 to 0.70 V versus Ag/AgCl. For example, the electroactivity of nitrite was observed only at potentials above 0.70 V versus Ag/AgCl. Therefore, these anions were not interferents in this analysis. The potential indicated for use in flow injection analyses by the amperometric method was 0.65 V versus Ag/AgCl for the large current signal and any interference.



**Fig. 3** Voltammograms obtained in the presence of interferent anions by linear voltammetry using Pt UME

### 4.3 Linearity

Figure 4 shows the relationship between the peak current ( $\mu\text{A}$ ) and concentration (in mg L<sup>-1</sup>) over the concentration range of 1–10 mg L<sup>-1</sup>. The curve has an excellent correlation coefficient ( $r = 0.9966$ ). According to the residual plot (Fig. 5), the residues fell in a random distribution around the zero line (straight line), and no pattern was observed. This means that the proposed linear model was adequate to describe the data. This graph also showed that the linear regression model was correct because the residues did not exceed 0.03  $\mu\text{A}$ , which was close to the baseline noise.

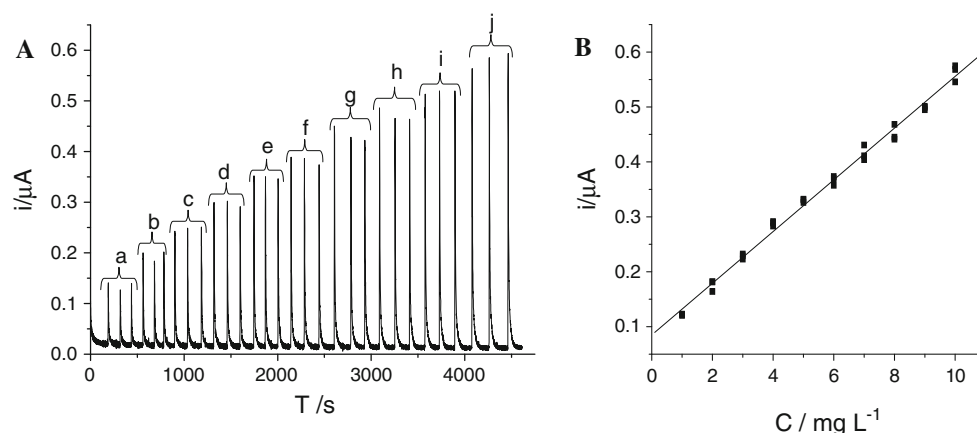
The Cochran test was applied to the amperometric method and the calculated value (0.2686) was also lower than the tabulated value (0.4450) for the curve over the range of 1–10 mg L<sup>-1</sup>. This result indicated homogeneous variances of the response with changing analyte concentration, which characterises homoscedastic behaviour. Therefore, a linear regression method can be used. Table 1 shows the data for different standard concentrations of iodide in chloride solution.

### 4.4 Limits of detection and quantification

Figure 6 shows the current versus time curve obtained for different concentrations of iodide (0.1, 0.2, 0.3 and 0.4 mg L<sup>-1</sup>) in an electrochemical flow cell, obtained using a decreasing order of iodide concentration. The last concentration of iodide analysed in the flow electrochemical cell with signal difference from the baseline was 0.2 mg L<sup>-1</sup>. This concentration value was considered to be the experimental iodide detection limit.

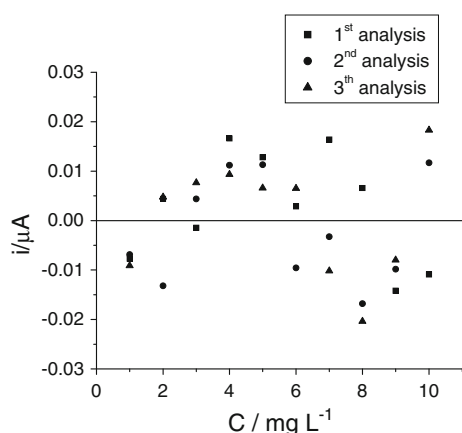
### 4.5 Recovery study

The recovery results showed in Table 1 were obtained from synthetic samples with different iodide concentrations. The amperometric method presented recovery values close to



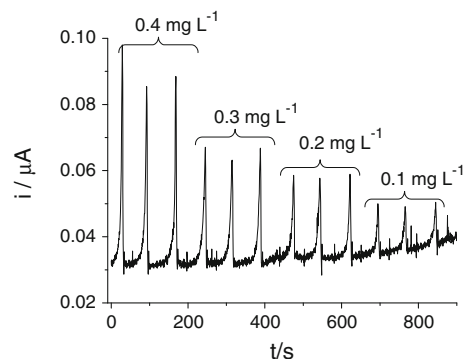
**Fig. 4** Amperometric (a) and analytical (b) curves recorded using several iodide concentrations in a  $29 \text{ g L}^{-1}$  chloride solution at  $0.65 \text{ V}$  using FIA and screen-printed electrodes. Iodide concentrations:

(a)  $1 \text{ mg L}^{-1}$ , (b)  $2 \text{ mg L}^{-1}$ , (c)  $3 \text{ mg L}^{-1}$ , (d)  $4 \text{ mg L}^{-1}$ , (e)  $5 \text{ mg L}^{-1}$ , (f)  $6 \text{ mg L}^{-1}$ , (g)  $7 \text{ mg L}^{-1}$ , (h)  $8 \text{ mg L}^{-1}$ , (i)  $9 \text{ mg L}^{-1}$  and (j)  $10 \text{ mg L}^{-1}$



**Fig. 5** Residue graph from the analytical curve obtained by the amperometric method using FIA and screen-printed electrodes

100 % and a relative error below 3 %. These results suggested a good performance considering the trace recovery iodide concentrations.



**Fig. 6** Current versus time curve for different concentrations of iodide in an electrochemical flow cell using screen-printed electrodes

Table 2 shows the recovery results obtained from real produced water samples fortified with iodide ranging from 2 to  $9 \text{ mg L}^{-1}$ . The method presented sample recovery values close to 102 % and a relative error below 2 %. The iodide content of this real produced water sample was

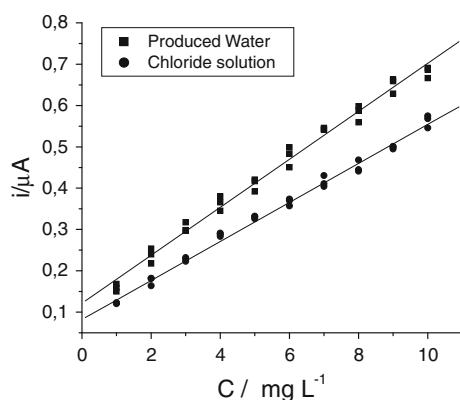
**Table 1** Data for analytical curve obtained from different standard concentrations of iodide in chloride solution by the amperometric method using FIA and screen-printed electrodes

$\text{I}^-$ concentration ( $\text{mg L}^{-1}$ )	1st signal ( $\mu\text{A}$ )	2nd signal ( $\mu\text{A}$ )	3rd signal ( $\mu\text{A}$ )	Average ( $\mu\text{A}$ )	$S^2$ ( $\mu\text{A}$ ) <sup>2</sup>	RSD (%)	Recovery (%)
1.0	0.1220	0.1228	0.1205	0.1218	$1.31 \times 10^{-6}$	1	94
2.0	0.1815	0.1639	0.1818	0.1757	$1.04 \times 10^{-4}$	6	99
3.0	0.2231	0.2289	0.2322	0.2281	$2.13 \times 10^{-5}$	2	102
4.0	0.2886	0.2831	0.2813	0.2844	$1.44 \times 10^{-5}$	1	105
5.0	0.3322	0.3307	0.3260	0.3296	$1.05 \times 10^{-5}$	1	103
6.0	0.3697	0.3573	0.3734	0.3668	$1.91 \times 10^{-4}$	2	100
7.0	0.4307	0.4110	0.4041	0.4153	$2.15 \times 10^{-4}$	3	100
8.0	0.4683	0.4450	0.4413	0.4515	$9.05 \times 10^{-4}$	3	98
9.0	0.4950	0.4993	0.5012	0.4985	$1.02 \times 10^{-5}$	1	98
10.0	0.5457	0.5683	0.5749	0.5630	$2.35 \times 10^{-4}$	3	101



**Table 2** Recovery results obtained for the amperometric method using FIA and screen-printed electrodes for real produced water fortified with iodide

Theoretical iodide concentration (mg L <sup>-1</sup> )	Measured iodide concentration (mg L <sup>-1</sup> )	Average	Standard deviation	Variance	Recovery (%)
2.0	2.3	2.0	0.25	0.0646	100
	2.0				
	1.7				
3.0	3.0	3.1	0.16	0.0646	103
	3.0				
	3.4				
4.0	4.5	4.2	0.25	0.0617	105
	4.2				
	3.9				
5.0	5.1	5.0	0.22	0.0478	100
	5.2				
	4.7				
6.0	5.7	6.1	0.34	0.1183	102
	6.2				
	6.5				
7.0	7.2	7.3	0.03	0.0010	104
	7.3				
	7.2				
8.0	8.2	7.9	0.28	0.0798	99
	7.5				
	8.0				
9.0	8.7	9.1	0.26	0.0702	101
	9.2				
	9.3				

**Fig. 7** Matrix effect study of the amperometric method using FIA and screen-printed electrodes

$2.1 \pm 0.3 \text{ mg L}^{-1}$ . The ion chromatography analysis of this sample showed  $1.74 \pm 0.06 \text{ mg L}^{-1}$  of iodide. Comparing the averages obtained by amperometry and ion chromatography, the calculated  $t$ -value (1.64) was found to be lower than the critical  $t$ -value (2.35) for the 95 % confidence level indicating that the hypothesis was accepted and the averages were equal.

#### 4.6 Precision

The amperometric method precision was evaluated by repeatability observing the standard deviation obtained for each concentration of analyte in the range of  $1\text{--}10 \text{ mg L}^{-1}$ . A good repeatability was verified (i.e. there were only small variations in the results of the triplicate analyses performed within a short time using the same conditions). The relative standard deviation values did not exceed 6 % variability (Table 1), which is considered acceptable for this type of technique. Thus, the proposed method can be considered to have good precision considering the type of analysis employed.

#### 4.7 Matrix effect

The matrix effect was evaluated by comparing the analytical curve slopes obtained in a real produced water sample and in  $29 \text{ g L}^{-1}$  chloride solution (Fig. 7). Comparing the variances obtained by amperometry, the calculated  $F$ -value (2.20) was found to be lower than the critical  $F$ -value (5.47) for the 99 % confidence level, indicating that the hypothesis was accepted and the variances were equal. The analytical

**Table 3** Electrochemical methods for iodide determinations

Technique	Electrode	Electrolyte	Sample	DL	Work range	Reference
Cathodic stripping square wave voltammetry	Static mercury drop electrode (HMDE mode)	0.1 % triton, sodium sulphite 1 mol L <sup>-1</sup>	Seawater	0.1 nM	0.24–0.71 μM	[10]
Constant-current stripping analysis (CCSA)	Tricresyl phosphate-based carbon-paste electrode (TCP-CPE)	Sodium chloride 2 mol L <sup>-1</sup>	Table salt	0.15 μM	0.4–20 μM	[11]
Linear-sweep voltammetry utilising current enhancement by redox cycling	Interdigitated microelectrode array (Pt-base)	Perchloric acid 0.1 mol L <sup>-1</sup>	Mineral water	0.3 μM	0.8–5 μM	[12]
FIA with amperometric detection	Boron-doped diamond thin film electrode (BDD)	Phosphate buffer 60 mmol L <sup>-1</sup> (pH 5)	Nuclear emergency tablets	0.01 μM	0.8–200 μM	[13]
FIA with amperometric detection	Platinum screen-printed electrodes (SPEs)	Sodium chloride 29 g L <sup>-1</sup>	Produced water of petroleum reservoir	0.2 mg L <sup>-1</sup> (or 1.6 μM)	1–10 mg L <sup>-1</sup> (or 7.9–79 μM)	Our study

curve slopes were also compared and the *t*-value calculated (2.19) was observed to be lower than the critical *t*-value (2.58) for the 99 % confidence level. Thus, these two curves had equal slopes and were not subject to matrix effects.

#### 4.8 Comparative study of electrochemical methods

Table 3 shows several electrochemical applications for the determination of iodide in different matrices. Although the lowest detection limit was not obtained in the present study compared to those presented in Table 3, the low working range of the proposed method is suitable for iodide analyses in water produced at petroleum reservoirs. Moreover, the platinum-based SPE used in the present amperometric method displays many advantages over other electrodes. The electrodes used in the methods shown in Table 3 present several disadvantages in terms of toxicity, high cost etc. and may require a step of modification. The advantages related to the performance of flow injection analysis combined with the practicality of SPEs justify the use of our method.

## 5 Conclusions

The amperometric method reported here using FIA and SPEs can be used for the determination of iodide in produced water samples. In the concentration range studied (1–10 mg L<sup>-1</sup>), the response was linear. This concentration range permits quantification of iodide at very low concentrations. The detection (0.2 mg L<sup>-1</sup>) and quantification (0.6 mg L<sup>-1</sup>) limits were considered good for this type of analysis. Moreover, the method was shown to have good recovery, precision and accuracy. Therefore, the developed amperometric method can be used to quantify iodide in produced water samples.

Comparison of the method reported here with those reported in the literature showed that this method allowed for faster analysis, did not require pre-treatment, used fewer reagents, employed the addition of samples directly to the analytical cell (without previous purification and separation), did not need preliminary preparation of the working electrode and had a low cost for both instrumentation and maintenance.

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